*Indian J. Phys.* **74B** (4), 297-300 (2000)

**I J P B**
— an international journal

# Investigations on the mobility and mass separation of ions in nonpolar liquids

B K Chatterjee

Department of Physics, Bose Institute, Calcutta-700 009, India
email barun@bosemain boseinst ernet in

*Received 4 May 1999, accepted 3 February 2000*

**Abstract** . An experimental method of studying ionic transport in silicone fluids is presented Preliminary measurements indicate the mobility of potassium to be 0 0004 $cm^2/Vs$ in 1cS octamethyl cyclotetra siloxane and indicate the mobility of copper ions to be $6.9 \times 10^{-6}$, $4.3 \times 10^{-6}$ and $3.8 \times 10^{-6}$ $cm^2/Vs$ in 1000 cS polydimethyl siloxane. A scheme to pulse and mass discriminate the ions are also presented

**Keywords** · Ion mobility, mass spectrometry, nonpolar liquids

**PACS Nos.** . 66.10.Ed, 07 75.+h

## 1. Introduction

In swarm experimentgs, *e.g.* using a drift tube [1], transport of ions in a gas provide valuable information on their mobility, diffusion constant, reaction coefficients with various neutral molecules, *etc.* In a drift tube, transport of ions in a gas can even separate various states (mainly metastable) of the drifting ions [2] and allows one to selectively study the reaction rate coefficients of the state separated ions. Swarm experiments hence, provide an invaluable tool to study ions, their transport and reaction, in gases. Swarm techniques are so reliable that one would be tempted to try to study all kinds of ions using these methods. However, the first major problem faced with swarm experiments is the generation of ions. Electron impact and discharge type ion sources can be reliably used to generate monatomic and some small molecular ions. For larger molecular ions (atomicity greater than 4) the neutral molecule is shattered into a large variety of fragment ions [3]. Some large ions can be generated by chemical ionization or by proton transfer by matching exoergicities but as the neutral molecule gets larger it gets more and more prone to dissociation even at small exoergicities. This severely limits the range of swarm experiments. To extend the range of masses of the ions used in swarm experiments, one usually resorts to higher gas pressures in the ion source. At these high gas pressures, the large collision frequency of the ions with the neutrals act to thermalize and stabilize the product ions thereby preventing them from dissociation. In its turn, high gas pressures provide their own inherent problems of extraction of ions, since extraction orifices go down in size with increasing pressures (pumping rate = puA/4; p - pressure inside drift tube, u - thermal velocity of buffer molecules, A - total area of exit orifices) and smaller orifices imply smaller ionic currents and dissociation of ions in the neighbourhood of the orifice.

To extend the versatile swarm techniques to larger and less studied molecules, transport of ions in a nonpolar liquid is studied. Nonpolar liquids do not solvate ions at room temperature. The liquid molecules however have a large frequency of collision with the ions thereby maintaining them in thermal equilibrium. Hence, nonpolar liquids form an excellent substitute for a gas at high pressure with respect to swarm experiments. As we shall observe, this provides a method to obtain the mass spectrum of very large molecules for which no *direct and simple method* for mass discrimination exists.

## 2. Experimental method

The experimental apparatus is described in Figure 1. A perspex tank contains the nonpolar liquid. Grooves in the

*Presently at the Department of Chemistry, University of Utah, Salt Lake City, UT 84112-0850, USA;
email : barunc@chemistry.chem.utah.edu

walls of the tank allow the positioning of various electrodes at measured positions. Positive ions studied using this

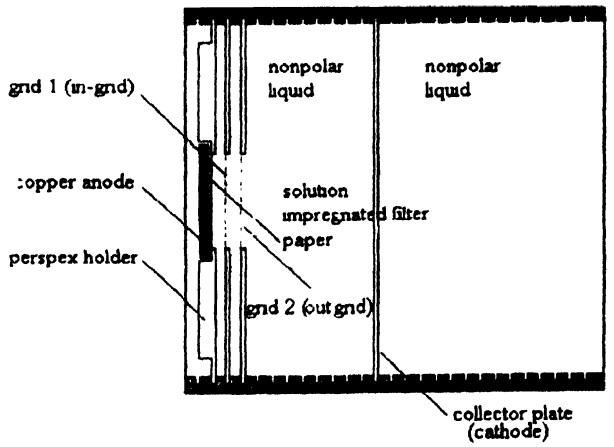


**Figure 1.** Diagram of the experimental setup

apparatus are generated at the anode. The anode is a copper disk (3 cm diameter, 0.4 cm thick) placed in contact with a filter paper impregnated with a solution of an electrolyte which is housed in a perspex plate such that the exposed impregnated filter paper is 2 cm in diameter. The ionic signal is detected using a seven-segment electrode (cathode) etched on a copper clad PVC board (used for making printed circuit boards). The central electrode is 2 cm in diameter. A split annular electrode pair (of inner and outer diameters of 2.1 cm and 3 cm respectively) surrounds the central electrode. This split electrode pair is surrounded in turn by four annular electrodes (of inner and outer diameters of 3 1 cm and 4 cm) as shown in Figure 2. The central electrode is intended for the study of mobility while the outer six electrodes are mainly to study the transverse diffusion of the ions (and could also be used for diagnostic purposes). This set-up can be used to study the continuous ionic current. The separation between the anode and the cathode (ion collecting electrode)

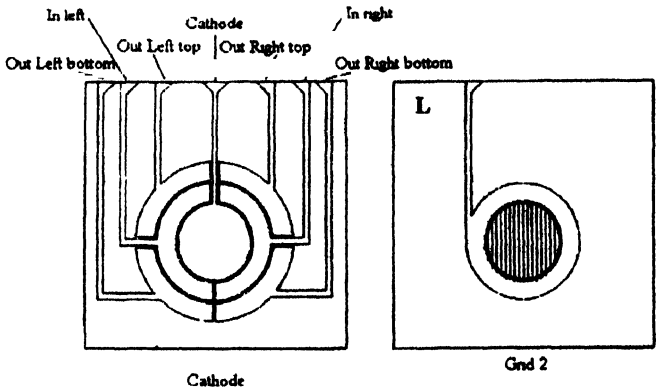


**Figure 2.** Diagram of the cathode and one of the grids etched onto a printed circuit board.

varied between 0.1 to 9.0 cm. In several experiments, a gas carbon anode disk was also used to reduce electrode corrossion but this design had problems with buildup of gases at the anode, which stops the ionic signal.

Grids were used to pulse the ionic current. These grids (one is shown in Figure 2) are designed using copper-clad PVC boards. They have a central hole 2 cm in diameter surrounded by a copper annulus on which an array of 0.014 ± 0.001 cm diameter copper wires (at a tension of 23.5 gmwt) are soldered at a separation of 0.175 ± 0.04 cm.

The entire set-up of the anode, cathode, grids and the perspex tank containing the nonpolar liquid is enclosed in a grounded metal tank to reduce electrical noise. In the continuous current mode, the grids were removed and a voltage is applied on the anode (the applied field is about 300 to 600 V/cm). The ionic signal from the central electrode of the cathode is connected to a storage oscilloscope and a chart recorder while the other six electrodes are grounded. When the voltage is applied on the anode, a transient displacement current is observed as a positive "spike". After a time lag from this spike the ionic current suddenly builds up reaching saturation. The time gap between the spike and the onset of the ionic current gives the drift time and from this the mobility of the ion is obtained.

The image charge of the drifting ions on the cathode causes the rise time of the ionic signal to be much larger and effectively reducing the drift time and making it more uncertain. This problem can be reduced, by placing a grid at about 0.1 cm from the cathode and applying an appropriate voltage on it, such that the electric field is constant from the anode to the cathode.

For pulsing the ionic current, two more grids are placed at a distance of 0.1 cm from the anode at a separation of 0.1 cm from each other. The grid close to the anode is labeled 1 and the other grid is labeled 2 (while gird 3 is to reduce the image charge problem). In the *pulse* mode, the voltages on the anode and the grids (the cathode is at ground potential) are such that the electric field is constant from grid 1 to the cathode and is reversed from the anode to grid 1. In the *charge* mode, the voltage on grid 1 is reduced below the anode voltage such that the magnitude of the electric field is constant from the anode to grid 1 and from grid 2 to the cathode but its direction is reversed from grid 1 to grid 2. Pulsing is obtained manually by switching the voltage on grid 1 in a pulse-charge-pulse-charge-sequence. It should be noted here that the introduction of each grid severely cuts down the ionic current thereby reducing the signal to noise ratio.

## 3. Experimental observation

To study the transport of potassium ions (the hydration of the ions could not be identified) in 1 cS octamethyl cyclotetra siloxane (OCMS) a solution of KI in water was placed on a filter paper, backed with a copper disk, which acted as the anode. Care was taken to avoid the filter paper from

dripping, and to avoid air bubbles from being trapped between the wet filter paper and the copper disk. The anode and the cathode were slowly lowered into the tank containing dehydrated and deionized OCMS such that bubbles trapped onto the surface of the electrodes immersed in the liquid are avoided. The experiment was performed in the direct mode (unpulsed mode) and grids were removed to maximize the ionic current. The separation between the anode the the cathode was 0.82 cm and the drift voltage was 300.7 V (drift field of 367 V/cm). A single ionic signal was observed to arrive after 5.5 s giving the drift velocity as 0.149 cm/s and a mobility of 0.0004 ± 0.0001 $cm^2/Vs$. The ionic current density was 42 $nA/cm^2$. The same experiment was repeated with KBr solution and the mobility of the positive ion was measured to be 0.0003 ± 0.00008 $cm^2/Vs$. The problem with both these electrolytes is that halogens accumulating between the copper plate and the filter paper severely cut down the ionic current and requiring the solution at the anode to be refreshed periodically.

In a separate experiment to study the mobility of copper ions in 100 cS polydimethyl siloxane, $CuSO_4$ was used in aqueous solution at the anode. This experiment had an added advantage that the ionic current could be obtained for prolonged intervals by dissolving the copper from the anode disk which is backing the moist filter paper. In this experiment the ionic current was pulsed and ions of mobility $6.9 \times 10^{-6}$, $4.3 \times 10^{-6}$ and $3.8 \times 10^{-6}$ $cm^2/Vs$ were observed. The ion with mobility of $4.3 \times 10^{-6}$ $cm^2/Vs$ was the most abundant. The grids need to be improved to reduce ionic leakage through them and hence obtain a better signal to noise ratio.

During the course of the measurement, the nonpolar (electrically nonconducting liquid) is rendered conducting and the resistivity of the liquid drops from its initial value of $2 \times 10^{11}$ ohm-m to an unacceptable level of $3 \times 10^9$ ohm m. At these lower levels of electrical resistivity, the leakage current is much larger than the ionic current giving a very poor signal to noise ratio. To rectify this problem, the solution is bilied to remove water micelles and deionized by prolonged application of high voltage (not high enough to cause electrical discharge though) by electrodes placed in the nonpolar liquid.

## 4. Mass separation of drifting ions

Ions drifting in a nonpolar liquid gains energy from the electric field and loses it in collisions with the molecules of the liquid. The rate of loss of kinetic energy ($E$) of a drifting ion is given [4–6] as

$$\frac{dE}{dt} - \frac{2e}{\mu(m+M)} E = E/\tau, \tag{1}$$

where $\tau$ is a relaxation time, $m$ and $M$ are the masses of the ion and neutral molecule respectively, $\mu$ is the mobility of the ion and $e$ is the charge of the ion. This formula is strictly valid at lower neutral densities (such that ion-buffer association reactions are negligible). At the neutral densities of the nonpolar liquid the mass term is no longer expected to be $m + M$ but some other linear combination of the two masses (at higher neutral densities the mass term is observed to be a linear combination of $m$ and $M$). $\tau$ is usually much larger than the mean collision period ($1/\nu$, where $\nu$ is the collision frequency) and is the thermalization time of a drifting ion. The equation governing the drift velocity of the ion is

$$\frac{du_d}{dt} + \frac{u}{2\tau} = \frac{\mu}{2\tau} X, \tag{2}$$

where $u_d$ is the drift velocity and $X$ is the electric field. Normally when $X$ is held constant, the time of flight in drift experiments are obtained as $t_f$, but if $X$ is suddenly switched off (after a time $t_1$, $t_1 < t_f$) for a brief period of time (a glitch of duration $w$) and then restored, the delay ($\delta$) encountered by the drifting ion is obtained as an implicit function of the duration of the glitch and $\tau$. This may be approximated to

$$\frac{\delta}{2\tau} \quad 1 - e^{-\frac{(t_f - t_1)}{2\tau}} \tag{3}$$

and from this $\tau$ may be obtained.

Using the pulsing scheme described above, $t_f$ (and hence $\mu$) may be obtained from the time gap between the starting spike and the centroid of the ionic pulse. A narrow negative pulse (of duration $w$) is introduced to grid 2 through a capacitor to zero the voltage on the grid. Using eq. (3), $\tau$ may be obtained from shift in the centroids ($\delta$) of the ionic pulses.

Since one expects $\tau/\mu$ to be a linear function of m/e, one can calibrate this linear function from various hydrations of a known drifting ion. This enables one to get a mass spectrum of the drifting ions from a spectrum of $\tau/\mu$. Reducing the duration of the glitch to the order of a femtosecond is the limitation, since $\tau$ is expected to be of that order for ordinary ions. This method is, however, very suitable for massive ions (*e.g.* ions of large biomolecules) where $\tau$ can be of the order of microseconds.

## 5. Conclusion

In conclusion we see that, in the absence of association reaction, transport of ions in a nonpolar liquid is similar to that in a gas at high pressure due to similarity in collision frequency. The preliminary measurements of mobility indicate that $e/\mu\eta$ for the potassium ions are 40 Å and for the copper ions are 23, 37 and 42 Å respectively ($\eta$ is the viscosity of the nonpolar liquid). We also present a method to mass discriminate ions and to obtain mass spectrum of very large molecular ions for which standard mass spectrometric methods can not be used.

## Acknowledgment

This research was funded by the Council of Scientific and Industrial Research, New Delhi.

### References

[1] J Heimerl, R Johnsen and M A Biondi *J. Chem. Phys.* **51** 5041 (1969)

[2] R Johnsen, M A Biondi and M Hayashi *J. Chem. Phys.* **77** 2545 (1982)

[3] B K Chatterjee, R Tosh and R Johnsen *Int. J. Mass Spectrom. Ion Phys* **103** 81 (1991)

[4] G H Wannier *Phys. Rev.* **83** 281 (1951)

[5] G H Wannier *Phys. Rev.* **87** 795 (1952)

[6] G H Wannier *Bell System Tech. J.* **32** 170 (1953)